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Molecular electronic structure of diphenyllead(IV) dichloride and comparison with diphenyltin(IV) dichloride by the SCF–MS molecular-orbital method

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Abstract

SCF–MS calculations on diphenyllead(IV) dichloride for two hypothetical monomers and the dimer of the Ph_2PbCl_2 polymeric compound elucidate the molecular electronic structure. Quasirelativistic wave functions and the Vosko–Wilk–Nusair (VWN) exchange-correlation potential were used. Ph_2PbCl_2 and Ph_2SnCl_2 have been compared to show the difference between the polymeric lead molecule, which is bonded through chlorine, and the monomeric tin molecule. The nuclear quadrupole resonance frequencies and asymmetry parameters of ^{35}Cl were calculated and interpreted. The asymmetry parameters and the molecular electronic structures of Ph_2PbCl_2 and Ph_2SnCl_2 highlighted the differences which result between the tin and lead molecules when diphenyllead(IV) dichloride polymerizes.

Introduction

Although Group IVB metal containing diorganometallic dihalides have been extensively studied, lead compounds are rarely mentioned [1]; perhaps the poisonous nature of the lead compounds discourages experimentalists, and the lack of experimental information causes neglect by theoreticians.

Diphenyllead(IV) dichloride is interesting because it has a polymeric chain structure [2,3], unlike the monomeric tin analogue [4]. To emphasize the difference between the intermolecular chlorine bonding in diphenyllead and diphenyltin dichlorides, the SCF–multiple scattering (SCF–MS) [5] theory was used. The details of the SCF–MS theory are published [5]. The SCF–MS results for diphenyltin(IV) dichloride (Ph_2SnCl_2) have been published [6]. The SCF–MS calculations were applied to the monomer and possible dimer of Ph_2SnCl_2. The monomer structure was from experiment; Greene and Bryan [4a] assumed that it had a C_{2v} structure of two isolated molecules with slightly different bond distances and angles, but with

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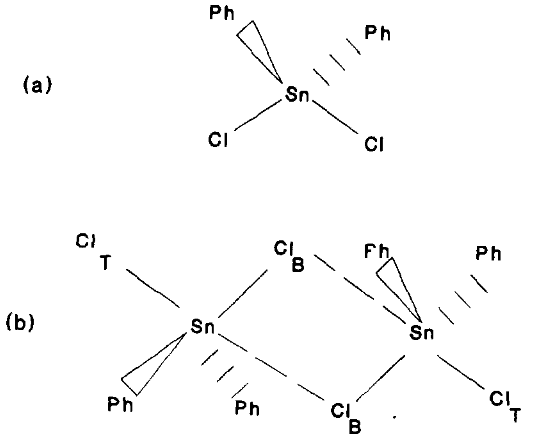


Fig. 1. Diagrams of (a) C_{2v} monomer and (b) C_{2h}"dimer". The bond lengths and bond angles were taken from ref. 4 and mean values are used for the monomer. In (b) the distances Sn–Cl_B, Sn $\cdots$ Cl_B and Sn–Cl_T are 2.357, 3.770 and 2.336 Å, respectively. The $Cl_B \cdots Cl_B$ distance was taken from ref. 4c as 4.284 Å.

identical geometry. The possible dimer was from experiment; Bokii et al. [4b] interpreted Greene and Bryan's results as if there were a dimeric structure with a short Sn–Cl_T bond of 2.336 Å and a long Sn–Cl_B bond of 2.357 which was assumed to reflect intermolecular bonding (Fig. 1). The molecular electronic structure of the diphenyltin dichloride monomer and possible dimer showed insufficient intermolecular chlorine interaction to hold two monomers as a "dimer". In this work the dimer $(Ph_2PbCl_2)_{n=2}$ and two hypothetical monomers, one with C_{2v} symmetry, as in the case of diphenyltin dichloride monomer, and the other with C_{2h} symmetry (Fig. 2) were calculated to study the difference in chlorine interaction compared to the diphenyltin dichloride "dimer", $(Ph_2SnCl_2)_2$. Here it will be analyzed why the intermolecular chlorine interaction is different in diphenyltin and diphenyllead dichlorides at their experimental geometries. The total energies are not calculated for different geometries, because these calculations are expensive and time consuming for systems like the dimer of Ph_2PbCl_2 which has 50 atoms and 396 electrons. The total energies from SCF–MS calculations are not reliable because of the muffin-tin approximation, but the wave functions are good [5c,7,8]. Non-muffin-tin methods like the discrete variational method (DVM–Xα) [9] and linear combination of atomic orbitals Xα method (LCAO–Xα) [10] give good total energies, but suffer from restrictions of a finite basis and numerical fitting procedures which are impractical for large molecules. The recent developed non-muffin-tin numerical Xα method [11] can give good total energies to diatomic molecules only.

The molecular electronic structure of Ph_2PbCl_2 has good SCF–MS wave function properties to describe the chemical bonding in Ph_2PbCl_2 compared to the tin analogue. The ^{35}Cl nuclear quadrupole resonance (n.q.r.) frequencies, ν, and the asymmetry parameter, η, are wave function properties helpful in analyzing the chemical bonding in chloride compounds. The SCF–MS programme [12] calculates the electric field gradients of the nuclei in the molecule. The n.q.r. frequencies in the chlorine compounds were calculated and found overestimated but parallel to experiment [6,13,14]. The ^{35}Cl n.q.r. frequencies and the asymmetry parameters of

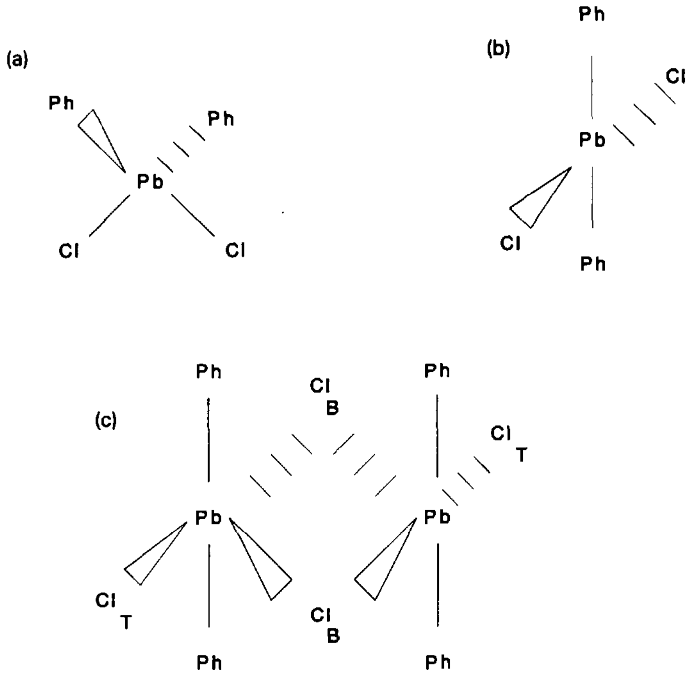


Fig. 2. Diagrams of the (a) C_{2v} "monomer", (b) C_{2h} "monomer" and (c) the dimer of diphenyllead(IV) dichloride. Bond angles and bonds lengths are from ref. 2 for the dimer, and are assumed for the two hypothetical monomers (a) and (b).

the diphenyllead dichloride were calculated to elucidate the chemical bonding and intermolecular chlorine interaction. The comparison of the asymmetry parameters of chlorine in the "monomers" and in the dimer is also given. The experimental measurements of ^{35}Cl n.q.r. frequencies are not available, but can be predicted from the calculations.

Computational details

The computational details of the diphenyltin dichloride calculation have been given [6]. The computational conditions for the diphenyllead dichloride calculations were the same as for the diphenyltin dichloride.

The experimental geometry for the diphenyllead dichloride is from crystal structure analysis [2]. The geometries of both hypothetical monomers are constructed from the dimer. The geometries of the "monomers" make qualitative comparison easy between the "free monomer" (C_{2v}), the "forced monomer" (C_{2h}) and the dimer. The schematic representation of the both C_{2v} and C_{2h} "monomers" and dimer of diphenyllead dichloride are in Fig. 2. Sphere sizes for the possible monomers and the dimer were chosen according to the Norman criteria [15] (Table 1). The partial waves, l, were taken as 4 for the outer sphere, 2 for Pb and Cl, 1 for C, and zero for H. The preferred Vosko–Wilk–Nusair (VWN) [16] exchange-correlation potential was used and not Slater's Xα exchange potential [5]. The calculations were performed with quasirelativistic wave functions [17] for Pb and Sn, because relativistic effects become important around Cu, $Z = 19$. In the quasirela-

Table 1

Sphere sizes used in SCF-MS calculation (a.u.)

"Monomer" (C_{2v})

R_{out}	R_{Pb}	R_{Cl}	R_{C_1}	R_{C_2} [a]	R_{C_3} [b]	R_{C_4}	R_{H_2} [c]	R_{H_3} [d]	R_{H_4}
11.5374	2.8126	2.7269	1.7690	1.7411	1.7428	1.7429	1.2973	1.2996	1.2996

"Monomer" (C_{2h})

R_{out}	R_{Pb}	R_{Cl}	R_{C_1}	R_{C_2} [a]	R_{C_3} [b]	R_{C_4}	R_{H_2} [c]	R_{H_3} [d]	R_{H_4}
12.4469	2.8508	2.8948	1.7296	1.7024	1.7041	1.7041	1.2683	1.2707	1.2708

Dimer

R_{out}	R_{Pb}	R_{Cl_B}	R_{Cl_T}	R_{C_1}	R_{C_2}	R_{C_3}	R_{C_4}	R_{H_2}	R_{H_3}	R_{H_4}
13.0616	2.8237	2.6997	2.8934	1.7229	1.7023	1.7022	1.7040	1.2682	1.2679	1.2707

[a] R_{C_6} is same as R_{C_2}. [b] R_{C_5} is same as R_{C_3}. [c] R_{H_6} is same as R_{H_2}. [d] R_{H_5} is same as R_{H_3}.

tivistic calculations only the large components, G_k of the radial wave functions are treated fully; they approach the nonrelativistic central-field wave function for small atomic numbers.

The $5d$ core orbital of Pb was treated as a valence orbital in the calculations, because the $5d$ core orbital of atomic Pb (−2.2588 Ry) is close to the valence orbitals of other atoms such as the $3s$ orbital of Cl (−1.8124 Ry), unlike the $5p$ of Pb (−6.461 Ry) [18]. After convergency is achieved with the quasirelativistic wave function for Pb the average energy level of the Pb ($5d$) in the dimer of Ph_2PbCl_2 moves to −2.0832 Ry which is very close to the energy of the next valence molecular orbital, $3a_u$ (−1.8805 Ry) but still far away from the closest core orbital, $5p$ of Pb (−6.8347 Ry).

Results and discussion

Electronic structure and bonding

There are 43 valence molecular orbitals in both monomers (C_{2v} and C_{2h}), the lowest lying five are lead($5d$) orbitals, and these correlate to the ten lead($5d$) and the remaining 76 orbitals of the dimer. The one-electron energies of $(Ph_2PbCl_2)_{n=2}$ lie between the highest occupied molecular orbital (HOMO), $19a_u$ (0.5500 Ry), and the lowest occupied valence molecular orbital above the Pb($5d$) orbitals, $3a_u$ (−1.8805 Ry). The dimer is greatly stabilized with respect to the either "monomer". The percentage distribution of these 76 molecular orbitals of $(Ph_2PbCl_2)_{n=2}$ among the atoms and atomic groups in the molecule follows the pattern in $(Ph_2SnCl_2)_2$. The percent composition of some of the lowest lying orbitals of $(Ph_2PbCl_2)_{n=2}$ and $(Ph_2SnCl_2)_2$ are in Table 2 and Table 3, respectively. The four lowest lying molecular orbitals, $3a_u$, $3b_g$, $4a_g$ and $4b_u$, following the ten Pb($5d$) core orbitals are the σ-bonding orbitals of the carbons in the phenyl groups. These are followed by the σ-bonding orbitals of bridge ($5a_g$ and $5b_u$) and terminal chlorine ($6a_g$ and $5b_u$) in $(Ph_2SnCl_2)_2$ (Table 3), but in the present $(Ph_2PbCl_2)_{n=2}$ (Table 2), the σ-bonding bridge chlorine orbitals ($5a_g$ and $5b_u$) are separated from the σ-bonding terminal chlorine orbitals ($8a_g$ and $8b_u$) by eight bonding orbitals of the phenyl groups. This means that the stabilization of the molecular orbital of the bridge

Table 2

The percentage compositions of some of the low-lying molecular orbitals of $(Ph_2PbCl_2)_{n=2}$

Orbital	2×Pb			$2\times Cl_B$			$2\times Cl_T$			24×C		20×H
	s	*p*	*d*	*s*	*p*	*d*	*s*	*p*	*d*	*s*	*p*	*s*
$8a_g$	3.35	0.59	0.25	0.35	0.06	0.01	91.45	0.07	0.03	2.03	1.43	0.37
$8b_u$	4.26	0.48	0.28	0.06	0.10	0.02	89.94	0.08	0.04	2.52	1.76	0.44
$7a_g$	0.00	0.08	0.00	0.00	0.02	0.00	0.08	0.00	0.00	74.68	15.00	10.16
$7a_u$	1.86	–	0.00	–	0.00	0.00	–	0.00	0.00	42.92	40.52	14.68
$5b_g$	–	0.00	0.26	–	0.01	0.00	–	0.00	0.00	74.76	14.80	10.16
$7b_u$	0.00	0.04	0.02	0.80	0.00	0.00	0.06	0.00	0.00	74.20	14.84	10.04
$6a_g$	2.50	0.04	1.94	5.28	0.04	0.00	0.48	0.04	0.02	70.05	13.12	6.50
$4b_g$	–	1.34	0.00	–	0.00	0.00	–	0.00	0.00	77.30	14.26	7.10
$4a_u$	1.35	–	0.00	–	0.01	0.00	–	0.00	0.00	77.27	14.25	7.12
$6b_u$	4.76	0.02	1.76	0.00	0.12	0.04	0.64	0.06	0.02	72.68	13.24	6.68
$5b_u$	0.00	0.88	1.72	96.26	0.00	0.00	0.08	0.02	0.00	0.64	0.24	0.16
$5a_g$	4.80	0.71	0.12	86.50	0.12	0.02	0.08	0.02	0.01	5.74	1.48	0.40
$4b_u$	1.21	0.00	3.15	0.00	0.04	0.01	0.05	0.02	0.01	81.01	11.92	2.59
$4a_g$	1.67	0.00	2.88	1.48	0.04	0.00	0.06	0.02	0.00	79.76	11.52	2.56
$3b_g$	–	0.78	0.00	–	0.00	0.00	–	0.00	0.00	84.96	11.64	2.60
$3a_u$	0.80	–	0.00	–	0.00	0.00	–	0.00	0.00	84.94	11.64	2.62

chlorine of $(Ph_2PbCl_2)_{n=2}$ is greater than that of the tin analogue. In the diphenyllead dichloride (Table 2), the average energy difference between the bridge chlorine ($5b_u$ and $5a_g$) and the terminal chlorine ($8a_g$ and $8b_u$) orbitals is 0.2017 Ry, whereas in the diphenyltin dichloride (Table 3) the difference between the bridge chlorine ($5b_u$ and $5a_g$) and the terminal chlorine ($6b_u$ and $6a_g$) bonding orbitals is 0.1368 Ry. This shows that the lead dimer has a stronger chlorine bridge than the tin "dimer". The percentage composition of these molecular orbitals are compared in both dimers, the terminal chlorine molecular orbitals, gerade and ungerade, are almost equal; for example the $8a_g$ and $8b_u$ of $(Ph_2PbCl_2)_{n=2}$ (91.45% and 89.94%) and the $6b_u$ and $6a_g$ of $(Ph_2SnCl_2)_2$ (81.86% and 82.94%). The percentage composition of the bridge chlorine molecular orbitals, gerade and ungerade, are not exactly equal, but the percent difference in the populations of the $5b_u$ and $5a_g$ of

Table 3

The percentage compositions of some of the low lying molecular orbitals of $(Ph_2SnCl_2)_2$

Orbital	2×Sn			$2\times Cl_B$			$2\times Cl_T$			24×C		20×H
	s	*p*	*d*	*s*	*p*	*d*	*s*	*p*	*d*	*s*	*p*	*s*
$6b_u$	5.10	2.22	1.54	2.54	0.20	0.04	81.86	0.68	0.26	4.24	1.00	0.36
$6a_g$	4.78	2.52	1.40	1.70	0.16	0.04	82.94	0.70	0.26	4.00	0.96	0.52
$5b_u$	3.74	1.90	1.56	89.40	0.36	0.14	1.56	0.18	0.08	0.48	0.16	0.40
$5a_g$	1.94	1.64	1.38	65.64	0.30	0.08	0.54	0.06	0.02	22.92	4.84	0.60
$3b_g$	–	0.32	0.20	–	0.00	0.00	–	0.00	0.00	84.12	12.76	2.56
$3a_u$	–	0.34	0.20	–	0.04	0.00	–	0.00	0.00	84.04	12.44	2.88
$4b_u$	0.76	0.08	0.20	0.12	0.04	0.02	0.12	0.02	0.00	83.64	12.36	2.60
$4a_g$	2.90	0.24	0.16	19.96	0.16	0.02	0.46	0.06	0.02	64.56	8.52	2.92

Table 4

Higher filled molecular orbitals of $(Ph_2PbCl_2)_{n=2}$

M.O.	$2 \times Pb$			$2 \times Cl_B$			$2 \times Cl_T$			$24 \times C$		$20 \times H$
	s	*p*	*d*	*s*	*p*	*d*	*s*	*p*	*d*	*s*	*p*	*s*
$19a_u$	0.00	–	0.00	–	0.00	0.04	–	0.46	0.02	0.00	99.48	0.00
$24a_g$	0.02	0.10	0.10	0.00	0.02	0.00	0.02	0.04	0.04	0.04	99.64	0.00
$19b_g$	–	0.00	0.00	–	0.34	0.00	–	0.64	0.02	0.00	99.00	0.01
$24b_u$	0.00	0.00	0.04	0.06	0.00	0.08	0.02	0.08	0.02	0.00	99.68	0.00
$18b_g$	–	0.00	1.42	–	0.00	0.05	–	0.66	0.04	0.00	97.82	0.00
$23b_u$	0.00	8.34	0.16	0.06	1.30	0.68	0.08	3.96	0.12	0.04	85.24	0.00
$18a_u$	0.00	–	1.56	–	0.46	0.10	–	1.18	0.04	0.00	96.64	0.00
$23a_g$	0.00	4.68	0.16	0.34	2.10	0.14	0.08	4.54	0.08	0.04	87.88	0.00
$17b_g$	–	0.08	0.14	–	0.00	0.00	–	95.72	0.00	0.11	3.81	0.14
$17a_u$	0.08	–	0.18	–	0.00	0.00	–	96.28	0.00	0.12	3.20	0.16
$22a_g$	0.00	0.68	0.38	0.04	1.02	0.04	0.00	97.24	0.00	0.04	0.52	0.04
$22b_u$	0.02	1.08	0.32	0.04	1.00	0.08	0.00	96.08	0.00	0.08	1.20	0.12
$21a_g$	0.32	7.12	4.10	0.12	7.34	0.18	0.04	69.76	0.14	0.72	9.88	0.24
$21b_u$	0.24	9.86	3.26	0.18	2.90	0.38	0.08	67.54	0.22	0.52	14.60	0.24
$16b_g$	–	0.02	1.31	–	0.00	0.05	–	1.83	0.03	0.02	96.75	0.00
$20b_u$	0.25	2.94	1.06	0.00	9.06	0.31	0.10	5.05	0.04	0.16	80.95	0.08
$16a_u$	0.09	–	0.93	–	6.56	0.06	–	1.08	0.02	0.00	91.22	0.03
$20a_g$	0.18	0.66	0.58	0.20	8.52	0.00	0.04	0.92	0.02	0.08	88.64	0.14

$(Ph_2PbCl_2)_{n=2}$ (about 9%) is not as large as that of $(Ph_2SnCl_2)_2$ (22%). The bonding orbitals between the central atom and the carbons of the phenyl groups and the bridge and terminal chlorines, lie above the orbitals given in Table 2 of $(Ph_2PbCl_2)_{n=2}$ and Table 3 of $(Ph_2SnCl_2)_2$ and below the higher filled valence

Table 5

Higher filled molecular orbitals of $(Ph_2SnCl_2)_2$

M.O.	$2 \times Pb$			$2 \times Cl_B$			$2 \times Cl_T$			$24 \times C$		$20 \times H$
	s	*p*	*d*	*s*	*p*	*d*	*s*	*p*	*d*	*s*	*p*	*s*
$19b_g$	–	0.00	0.02	–	0.18	0.06	–	0.04	0.00	0.00	99.68	0.00
$24b_u$	0.00	0.02	0.04	0.06	0.02	0.04	0.00	0.00	0.00	0.00	99.72	0.04
$19a_u$	–	0.00	0.02	–	0.14	0.10	–	0.06	0.00	0.04	99.64	0.00
$24a_g$	0.00	0.18	0.00	0.08	0.02	0.06	0.00	0.02	0.00	0.00	99.56	0.04
$18b_g$	–	0.02	0.72	–	0.14	0.00	–	0.14	0.00	0.04	98.88	0.00
$18a_u$	–	0.04	0.86	–	0.00	0.12	–	0.16	0.04	0.04	98.68	0.00
$23a_g$	0.06	0.92	1.16	0.02	0.80	0.08	0.04	0.54	0.06	0.04	95.76	0.04
$23b_u$	0.18	1.92	1.50	0.22	0.52	0.04	0.06	1.02	0.12	0.04	94.08	0.00
$17b_g$	–	0.02	0.18	–	0.90	0.02	–	4.00	0.00	0.00	94.80	0.00
$17a_u$	–	0.30	0.60	–	0.54	0.06	–	3.60	0.00	0.08	94.56	0.24
$22b_u$	0.12	0.26	1.30	0.10	0.50	0.08	0.00	2.46	0.00	0.04	95.04	0.12
$22a_g$	0.18	0.12	1.46	0.00	1.76	0.02	0.00	2.66	0.00	0.12	93.24	0.40
$16b_g$	–	9.92	2.46	–	2.58	0.10	–	44.84	0.08	1.84	11.68	4.68
$16a_u$	–	8.66	2.34	–	0.18	0.06	–	56.06	0.06	1.48	27.80	3.48
$21b_u$	0.24	0.20	1.34	0.04	3.90	0.04	0.00	92.48	0.00	0.08	1.56	0.08
$21a_g$	0.02	0.24	1.20	0.06	2.52	0.08	0.00	93.74	0.00	0.00	1.92	0.08

orbitals which are given in Table 4 and Table 5 for $(Ph_2PbCl_2)_{n=2}$ and $(Ph_2SnCl_2)_{n=2}$, respectively.

In these organometallics $(Ph_2PbCl_2)_{n=2}$ and $(Ph_2SnCl_2)_2$ compounds, the higher filled valence molecular orbitals belong to the nonbonding phenyl C(p) orbitals, unlike the inorganic bridged compound Al_2Cl_6 [14] where the higher filled orbitals belong to the nonbonding terminal Cl(p) orbitals. In the strong lead dimer (Table 4) there are eight nonbonding phenyl C(p) orbitals followed by six $Cl_T(p)$ orbitals and just below these orbitals are four phenyl C(p) orbitals. However in the weak tin "dimer" (Table 5) all twelve phenyl C(p) orbitals lie above the terminal $C_T(p)$ orbitals. As it is shown in Tables 4 and 5, the percentages of the $Cl_T(p)$ orbitals in the weak tin "dimer" are smaller than those in the lead dimer. Below these $Cl_T(p)$, the $Cl_B(p)$ orbitals occur and are distributed over the bonding orbitals.

The importance of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for analysing the nature of the chemical bonding, geometries, and reactivity has been recognized [19,20,21]. The stability of the molecules is frequently attributed to the HOMO, LUMO interaction [19]. The predicted stability of molecules, including the inorganic molecule, B_2H_6 was calculated by an *ab-initio* molecular orbital theory using the HOMO, LUMO interaction without any energy interpretation [22]. The electron delocalization caused by the HOMO and LUMO was considered the most important contribution to organic reactions [20].

Consequently, the HOMO and LUMO of the monomers and the dimers of Ph_2PbCl_2 and Ph_2SnCl_2 are used to analyse the difference in chemical bonding between the tin and lead analogues.

The HOMO is a non-bonding carbon(p) of the phenyl groups in the monomers and the dimers of the diphenyllead and diphenyltin dichloride; however, the LUMO, although antibonding in the molecules, is different in nature in diphenyllead dichloride and diphenyltin dichloride (Table 6). The striking change in the LUMO is between the C_{2v} and C_{2h} "monomers", and the dimer for diphenyllead dichloride; the d-contribution of lead is insignificant in the C_{2v} "monomer" where lead is tetrahedral coordinated, it increases to 18 percent in the C_{2h} "monomer" in which the monomer is prepared to become the dimer; in the dimer, the lead(d) contribution is almost the same as in the C_{2h} "monomer" 18%. The empty d orbitals allow lead to accept more electrons, form more bonds and complete the octahedral coordination in the polymer. Whereas from Table 6, it is seen that the d-contribution in the LUMO of the monomer and the "dimer" of diphenyltin dichloride is insignificant; that the central tin atom is tetrahedral in the monomer and in the "dimer" [6]; thus tin cannot accept extra bonds or any other interaction in the "dimer" over the monomer. The contour diagrams of both antibonding LUMO's of lead and tin dimers are given in Fig. 3 for visual comparison.

Figure 4 compares the HOMO and LUMO in the monomers and dimers of the Ph_2PbCl_2 and Ph_2SnCl_2 molecules. In both dimers the HOMO and LUMO are stabilized with respect to the HOMO and LUMO of the monomers. The slight stabilization in the valence molecular orbitals of the dimer can be attributed to the increased sphere volume of the dimer with respect to the monomer; how much stabilization is caused by the increased sphere volume cannot be easily analysed. Despite the increased sphere volume, if the interaction were strong it would show up in the valence molecular orbitals of the dimer. When two monomers, like AlX_3,

Table 6

The comparison of the percentage compositions of the LUMO's of the monomers and the dimers of Ph_2PbCl_2 and Ph_2SnCl_2

a. Ph_2PbCl_2

"Monomer" (C_{2v})

LUMO	Pb			2×Cl			12×C		10×H
	s	*p*	*d*	*s*	*p*	*d*	*s*	*p*	*s*
$15a_1$	13.20	14.01	2.08	4.40	23.30	10.52	5.42	26.28	0.88

"Monomer" (C_{2h})

LUMO	Pb			2×Cl			12×C		10×H
	s	*p*	*d*	*s*	*p*	*d*	*s*	*p*	*s*
$15a_g$	12.54	–	18.54	0.62	6.46	0.98	11.60	47.93	1.34

Dimer

LUMO	2×Pb			$2\times Cl_B$			$2\times Cl_T$			24×C		10×H
	s	*p*	*d*	*s*	*p*	*d*	*s*	*p*	*d*	*s*	*p*	*s*
$25a_g$	10.14	6.98	17.96	0.42	2.08	0.74	0.16	2.00	0.22	10.48	47.44	1.40

b. Ph_2SnCl_2

Monomer

LUMO	Sn			2×Cl			12×C		10×H
	s	*p*	*d*	*s*	*p*	*d*	*s*	*p*	*s*
$15a_1$	15.10	13.34	1.26	4.22	22.90	14.94	4.96	22.58	0.74

"dimer"

LUMO	2×Sn			$2\times Cl_B$			$2\times Cl_T$			24×C		20×H
	s	p	d	s	p	d	s	p	d	s	p	s
$25b_u$	14.68	14.86	1.40	2.14	12.38	11.76	1.36	8.94	4.28	4.24	23.12	0.88

combine together to form a strong dimer Al_2X_6, some of the valence orbitals are stabilized and some of them destabilized with respect to their monomer counterparts; despite the volume increase in the dimer, the effect of the strong bridging interaction in the dimer of AlX_3 is observable [14,23] since if a strong interaction exists in the dimer, it is reflected in the valence molecular orbitals including the HOMO and the LUMO. The SCF–MS calculations on AlX_3 [23], and Al_2X_6 [14] showed that the HOMO and LUMO energy difference in strong dimers to be smaller than the HOMO and LUMO energy difference of their monomers.

The stabilization of the HOMO and LUMO is different in the two dimers, Ph_2PbCl_2 and Ph_2SnCl_2. In the Ph_2SnCl_2, Fig. 4b, the stabilization of the HOMO and LUMO of the "dimer" with respect to the HOMO and LUMO in the monomer are the same (0.10 Ry). The energy difference between HOMO and LUMO in the "dimer" and in the monomer is also the same (0.12 Ry). However, in Ph_2PbCl_2, Fig. 4a, the stabilization of the HOMO and LUMO of the dimer with respect to the HOMO and LUMO in the C_{2h} "monomer" is different by 0.07 and 0.09 Ry, respectively. Similarly the stabilization of HOMO and LUMO of the C_{2h} "monomer" with respect to those in the C_{2v} "monomer" is different by 0.05 and 0.10 Ry,

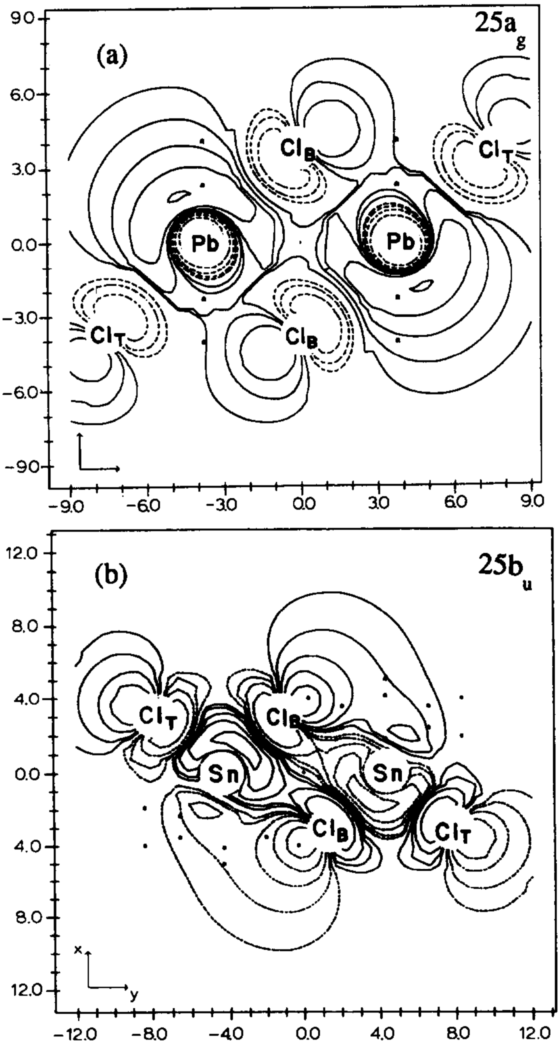


Fig. 3. The wave function contour diagrams on the chlorine-metal plane for the LUMOs of (a) $(Ph_2PbCl_2)_{n=2}$ ($25a_g$) and (b) $(Ph_2SnCl_2)_2$ ($25b_u$). The carbon and hydrogen positions of the phenyl groups are shown by small dots. The contour values, $(\text{electrons}/a_0^3)^{1/2}$, starting from outermost contour are ±0.005, ±0.01, ±0.02, ±0.04, ±0.08, and ±0.16. Positive contours are solid lines and negative contours dashed lines.

respectively. The energy difference between the HOMO and LUMO of the dimer is not equal to that in the "monomers", being 0.05 Ry compared to the C_{2h} "monomer" (0.07 Ry) and the C_{2v} "monomer" (0.12 Ry). These comparisons give qualitative information about the interactions in the Ph_2PbCl_2 and Ph_2SnCl_2 molecules. It has been proved [6] from the Mössbauer isomer shift and the quadrupole splitting of ^{119}Sn and n.q.r. parameters of ^{35}Cl in the "dimer" of Ph_2SnCl_2 that, this "dimer" has no significant interaction through the intermolecular bridge chlorine; the presence of a second monomer does not change the nature of the bonding in either monomer. It is now apparent that the equal stabilization of the HOMO and LUMO

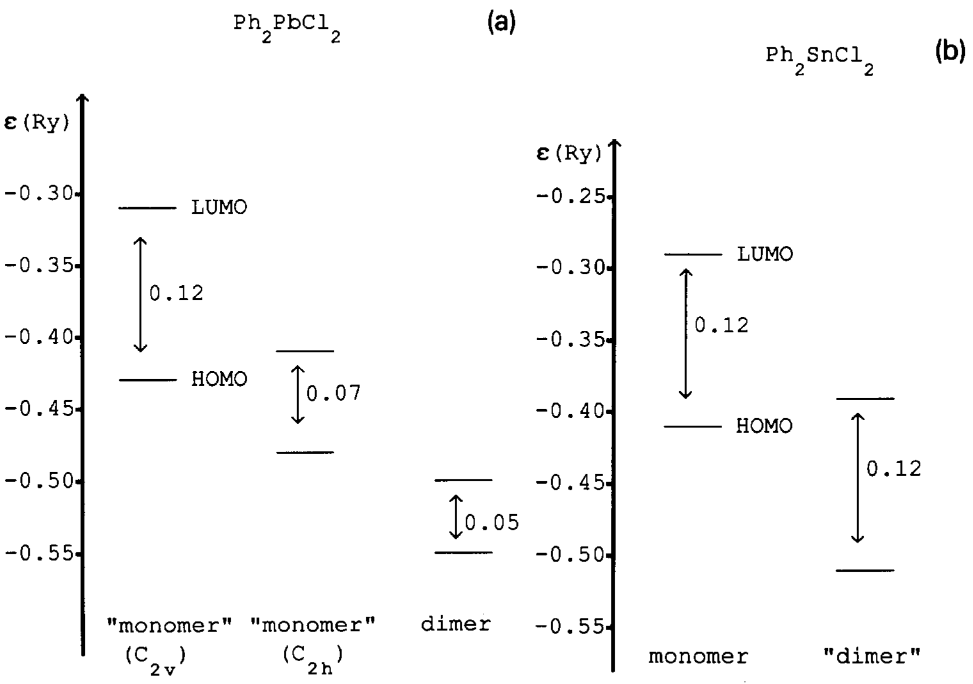


Fig. 4. Comparison of the HOMO and LUMO levels (in Ry) of (a) Ph_2PbCl_2 and (b) Ph_2SnCl_2.

of the "dimer" of Ph_2SnCl_2 with respect to the monomer and the equal energy difference between HOMO and LUMO of the "dimer" and the monomer also supports Ph_2SnCl_2 being a monomer. Consequently for the Ph_2PbCl_2 it follows that the unequal stabilization of the HOMO and LUMO of the dimer with respect to the HOMO and LUMO levels of both "monomers" and the unequal (smaller) energy difference between the HOMO and LUMO of the dimer compared to the "monomers" reflects the change in the chemical bonding in the dimer. The presence of a second monomer is felt by both monomers in the dimer.

The comparisons of the dimers of lead and tin therefore show that the lead dimer prefers to have more bonds and polymerize while the tin remains as a monomer. These ideas are supported by the relativistic effects which are more profound in lead than tin. Table 7 gives the comparison of the nonrelativistic and the quasirelativistic one-electron energies of core levels of Pb and Sn in $(Ph_2PbCl_2)_{n=2}$ and $(Ph_2SnCl_2)_2$, respectively. As the principal quantum number increases the relativistic *s* and *p* orbital stabilization and *d* orbital destabilization increases. These relativistic effects can also be found for the atoms [24]. By analyzing Table 7 it is expected that 6*s* of Pb will be more stabilized accompanied by the relativistic 6*s* contraction; this contraction is absent in the tin compound [25]. The effects of the relativistic Pb(6*s*) contraction in some organolead compounds were given by Pyykkö [26]. Therefore it can be expected that the molecular orbitals which have Pb(6*s*) contribution will lie lower in energy. The relativistic destabilization and the radial expansion of the 5*d* orbital will cause it to lie higher and eventually be involved with bonding. All these effects are much greater in the Pb than the Sn compound, and it can be expected that the Pb compound will have a *d* orbital contribution to the bonding. The

Table 7

Comparison of nonrelativistic and quasirelativistic one-electron energies of core levels of Pb and Sn in $(Ph_2PbCl_2)_{n=2}$ and $(Ph_2SnCl_2)_2$, respectively (Ry)

Orbital	Non-rel.	Quasi-rel.	%
$(Ph_2PbCl_2)_{n=2}$			
1s	5802.6314	6352.5169	9.5
2s	978.1486	1138.3194	16.4
2p	942.2177	996.4565	5.8
3s	233.5210	273.7420	17.2
3p	216.3683	231.8845	7.2
3d	184.2478	183.4740	−0.4
4s	51.9790	62.1306	19.5
4p	44.4538	48.0454	8.1
4d	30.5333	30.0882	−1.46
4f	11.6591	10.3033	−11.63
5s	8.9076	10.8371	21.7
5p	6.3819	6.8347	7.1
5d [a]	2.3227	2.0833	−10.3
$(Ph_2PbCl_2)_{n=2}$			
1s	2053.9068	2131.2691	3.8
2s	303.4374	322.0020	6.1
2p	284.0302	289.6769	2.0
3s	58.6521	62.4173	6.4
3p	50.6356	51.8003	2.3
3d	35.7135	35.2459	1.3
4s	9.5208	10.2420	7.6
4p	6.8562	7.0205	2.4
4d [a]	2.4615	2.3541	−4.4

[a] Average of the 10(*d*) orbitals.

availability of the *d* orbitals in the Pb will make the Pb compound octahedral rather than tetrahedral.

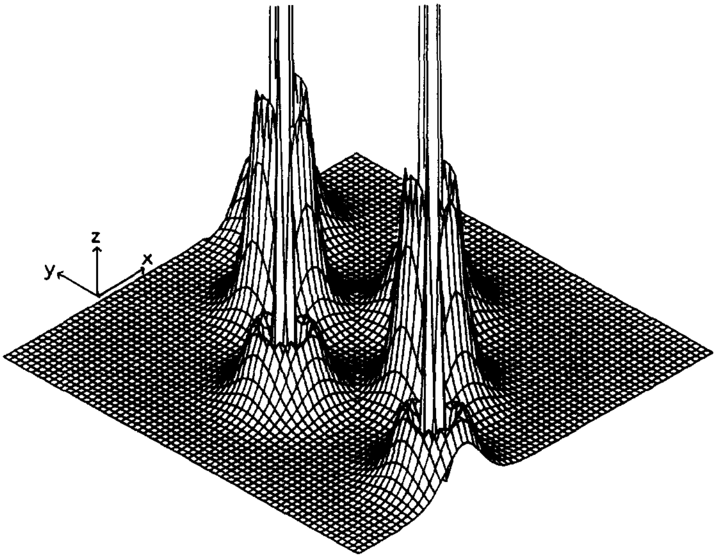
The other relativistic effect which is not available in the quasirelativistic calculation is the spin–orbit effect. The relativistic spin–orbit effects on the bonding, dissociation energies and the ionization potentials were reviewed by Pyykkö [26]. The lowering effect of spin–orbit coupling on the dissociation energies of Pb_2, PbO and PbH was calculated by Balasubramanian et al. [27]. In our molecules, it is possible that the Pb–Cl bond which is more ionic than the Sn–Cl bond, which is discussed below, would be affected more than the Sn–Cl bond by the spin–orbit coupling. Thus, the spin–orbit coupling could cause weakening of the Pb–Cl bond; however, it could leave Pb–Cl bridged compared to the almost no bridged Sn–Cl bond.

The spin–orbit splittings were also calculated for the lead and tin halides and found larger for the lead compound by Balasubramanian [28,29]. Due to the spin–orbit splitting, we can expect the Pb(5*d*) involvement in the bonding to be much larger because the upper levels of the Pb(5*d*) will split and lie much higher than the barycenter.

The total charge density maps for $(Ph_2PbCl_2)_{n=2}$ and $(Ph_2SnCl_2)_2$ are in Fig. 5a and 5b. The electron charge density is most dense at the central lead, tin and chlorine nuclei and becomes less dense away from the nuclei. While Fig. 5a shows

(a)

$(Ph_2\,PbCl_2)_{n=2}$



(b)

$(Ph_2\,SnCl_2)_2$

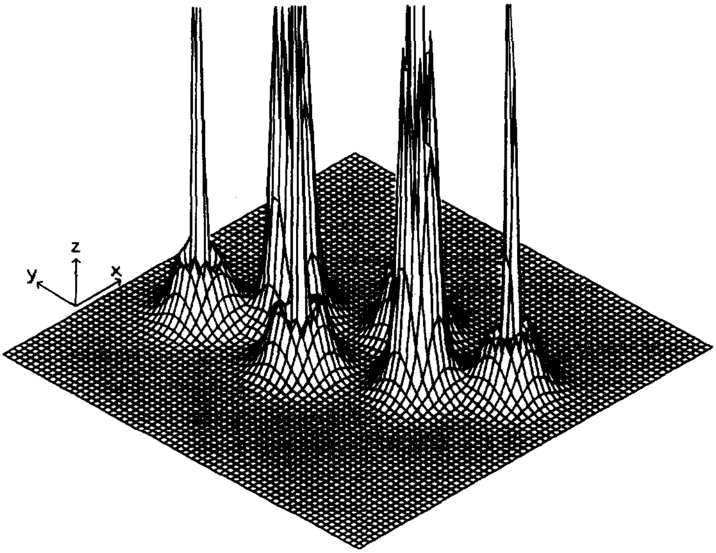


Fig. 5. The charge density plot on the chlorine–metal plane for (a) $Ph_2PbCl_2)_{n=2}$ and (b) $(Ph_2SnCl_2)_2$.

Table 8

Total charge distribution

	Central Metal	Cl_B	Cl_T	Ph
$(Ph_2PbCl_2)_{n=2}$	81.40	17.40	17.58	40.79
$(Ph_2SnCl_2)_2$	49.39	17.05	17.14	41.16

the strong bridging through the chlorines, Fig. 5b shows no such interaction. The total electron distributions of both lead and tin containing dimers among atoms and groups are in Table 8. In both dimers bridging chlorines (Cl_B) have slightly lower charge than the terminal chlorines (Cl_T). The lead dimer has a larger charge on both chlorines (Cl_B and Cl_T) compared to the tin "dimer", so that the metal–chlorine bond of Ph_2PbCl_2 is more ionic than in Ph_2SnCl_2 [1]. Because the electronegativity of carbon (2.55) is higher than lead (2.33) or tin (1.96) [30], and the electronegativity difference between carbon and lead is less than that between carbon and tin, the phenyl groups in the lead dimer attract less electrons than in the tin analogue (Table 8).

^{35}Cl *nuclear quadrupole coupling*

Nuclear quadrupole resonance (n.q.r.) spectroscopy studies chemical bonding in chlorine-containing compounds through the *p*-electron distribution in the valence shell which causes the n.q.r. frequencies. The n.q.r. frequency ν of ^{35}Cl is calculated using equation [31]

$$\nu = \tfrac{1}{2}\left(e^2 q_z Q/h\right)\left(1 + \eta^2/3\right)^{1/2}, \tag{1}$$

where $(e^2 q_z Q/h)$ is the nuclear quadrupole coupling constant in which eQ is the nuclear quadrupole moment, -0.082 barns for ^{35}Cl [32], and eq_z $(= V_{zz})$ is the maximum principal component of the electric field gradient. The electric field gradients are calculated from the one-electron properties using the charge partitioning method of Case, Cook and Karplus [33]. In eq. 1 the asymmetry parameter η $(= |V_{xx} - V_{yy}|/V_{zz})$ gives the deviation from cylindrical symmetry. The asymmetry parameter η describes the change in the chemical bond going from the (C_{2v}) "free monomer" to the (C_{2h}) "forced monomer", and to the dimer. The calculated asymmetry parameters η are in Table 9. In the strong dimer the asymmetry parameters η of the bridge chlorines (η_B) are larger [34] than those of at the terminal chlorine (η_T) but when the dimer is a "free" dimer, the asymmetry parameters η of terminal chlorines and their monomer chlorines are almost equal and close to zero [6,14,34]. In Table 9, the asymmetry value of the monomer

Table 9

The calculated nuclear quadrupole asymmetry parameters, η, of ^{35}Cl of Ph_2PbCl_2

Ph_2PbCl_2	η	η_B	η_T
"Monomer" (C_{2v})	0.03	–	–
"Monomer" (C_{2h})	0.23	–	–
Dimer	–	0.26	0.21

chlorine is close to zero in the "free monomer" (C_{2v}) and increases as we go to the "forced monomer" (C_{2h}). In the dimer, η_T is smaller than η_B, as expected, but not close to the "free monomer" value; therefore these terminal chlorines are the bridge chlorines for the continuing polymer. This idea is supported by the nonzero η value of the "forced monomer", chosen to look as if it were in the polymer.

SCF–MS calculations usually overestimate the n.q.r. resonance frequencies for ^{35}Cl, ^{79}Br and ^{127}I in aluminium trihalide dimers [14]. However, it has been found that the calculated n.q.r. frequencies of halides parallel experiment [13,14]. There are no n.q.r. measurements for ^{35}Cl in the Ph_2PbCl_2 molecule; however, the ^{35}Cl frequencies can be predicted from the experimental measurements for the Group IVB tetrachloride molecules [34]. The chlorine frequencies decrease as the central atom gets heavier and the addition of less electronegative ligands such as methyl, butyl and phenyl also decreases the chlorine frequencies. Therefore, the experimental n.q.r. frequencies of ^{35}Cl in diphenyllead dichloride will be expected to be lower than in the tin molecule, diphenyltin dichloride (average 17.67 MHz for the bridge chlorine and 18.40 MHz for the terminal chlorine [6.35]). In the lead dimer it is estimated to be 11.66 MHz for the bridge and 12.65 MHz for the terminal chlorine. With the reservation that the calculated n.q.r. frequencies are always 30 to 50% overestimated and considering the increased ionic character of the lead–chlorine bond, the polycrystalline Ph_2PbCl_2 polymer will have reduced n.q.r. frequencies from the calculated values. The experimental ^{35}Cl n.q.r. frequency would be around 5 to 6 MHz. Since Ph_2PbCl_2 is polymeric there will only be a single frequency characteristic of bridge chlorines.

Conclusion

The present work compares a detailed SCF–MS analysis of the molecular electronic structures of diphenyllead(IV) dichloride with diphenyltin(IV) dichloride. The electronic structure and chemical bonding in the Ph_2PbCl_2 "monomers" and dimer, together with their chlorine n.q.r. asymmetry parameters η and the comparison with the results for Ph_2SnCl_2 suggest that the terminal chlorines of Ph_2PbCl_2 act as bridge chlorines in the polymer. The population analysis of the Ph_2PbCl_2 and Ph_2SnCl_2 dimers shows Ph_2PbCl_2 to have strong intermolecular chlorine interaction; the total density map of the dimer of diphenyllead dichloride supports this.

Experimentalists should search for the n.q.r. frequency of ^{35}Cl in the Ph_2PbCl_2 around 5 to 6 MHz.

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